De kristalstructuren van (NSF)4, alpha(NSOCl)3 en (NSCl)3

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SUMMARY

In organic aromatic compounds delocalization of the π-electrons is associated with overlapping p_π-orbitals on neighbouring carbon atoms. It was pointed out first by Craig on the basis of simple molecular orbital theory that in inorganic ring systems e.g. $(NPCl_2)_n$, in which first and second row elements alternate, a similar π-electron delocalization may occur by overlap of p_π- and d_π-orbitals. The theory of this p_π-d_π delocalization (CRAIG c.s., DEWAR c.s., DAVIES CRUICKSHANK) is reviewed in chapter II of this thesis. Several phosphonitrilic molecules containing $(NP)_3$ or $(NP)_4$ rings have been studied by X-ray diffraction recently. In each of these molecules the P—N bond lengths within the ring are equal and short. The actual length of the P—N bonds and the geometry of the ring in molecules with $(NP)_4$ rings depend on the substituents on the phosphorus atoms.

In the introduction and in chapter I it is pointed out that very little was known about the structures of the analogous compounds with $(NS)_n$ rings (thiazyl halides). For these compounds as well as for the phosphonitrilic compounds, delocalization of the p_π-d_π bonds had been predicted. In order to establish the character of the S—N bonds and the influence of the substituents on the bond lengths and angles in the ring, we determined the crystal structures of $(NSF)_4$, $\alpha(NSOCl)_3$ and $(NSCl)_3$ by means of X-ray diffraction.

Chapter III deals with the experimental details of the structure determinations. Crystals of $(NSF)_4$ were kindly provided by Prof. Glemser (Göttingen); those of $\alpha(NSOCl)_3$ and $(NSCl)_3$ were prepared according to GOEHRING (1957). All intensities were measured with a densitometer on integrated equi-inclination Weissenberg photographs. Use was made of the multiple-film technique. The photographs of $(NSF)_4$ were taken with nickel-filtered copper radiation, those of $\alpha(NSOCl)_3$ and $(NSCl)_3$ with zirconium-filtered

molybdenum radiation. The crystals of $(NSCl)_3$ were cooled to —130° C by means of a stream of evaporated liquid nitrogen. Since the crystals of $(NSCl)_3$ and $\alpha(NSOCl)_3$ were small (diameter 0.2 mm; μ appr. 18 cm^{-1}) no correction for absorption was applied. The intensities obtained from $(NSF)_4$ were approximately corrected for absorption, by assuming the crystals to be cylindrical; for the different crystals the value of μR was between 0.4 and 0.6. Reflections were obtained to $\sin\vartheta/\lambda = 0.65$ $Å^{-1}$ for $(NSF)_4$ and $\alpha(NSOCl)_3$, and to $\sin\vartheta/\lambda = 0.80$ $Å^{-1}$ for $(NSCl)_3$. The accurary of the intensities was estimated by comparing the intensities of the same reflections, recorded on Weissenberg photographs about different axes. The value of

$$\sum_{hkl} \sum_{i} \| F_i|^2 - |F_m|^2| / \sum_{i} |F_i|^2$$

in which $|F_i|^2$ and $|F_m|^2$ are respectively the individual and mean vauleus of the corresponding intensities, was 0.054 for 184 pairs of reflections of $\alpha(NSOCl)_3$ and 0.041 for 348 pairs of reflections of $(NSCl)_3$.

The structure determinations of $(NSF)_4$, $\alpha(NSOCl)_3$ and $(NSCl)_3$ are described in chapter IV, V, and VI. The approximate structures of $(NSF)_4$ and $(NSCl)_3$ could be determined from Patterson projections; for $\alpha(NSOCl)_3$ the approximate structure was deduced from the three-dimensional Patterson synthesis. The structure of $(NSF)_4$ was refined by three-dimensional difference Fourier syntheses. For the calculation of the structure factors the temperature factors of the atoms were assumed to be isotropic. The structures of $\alpha(NSOCl)_3$ and $(NSCl)_3$ were refined by the method of least-squares; in the available program only isotropic temperature factors could be taken into account. During these three-dimensional refinements the centrosymmetric space groups *Pnma* and $P2_1/m$ for $\alpha(NSOCl)_3$ and $(NSCl)_3$ respectively, were adopted. In these space groups the molecules have a special position on a mirror plane. The structure of $\alpha(NSOCl)_3$ was also refined anisotropically by three-dimensional difference Fourier syntheses; the coordinates are compared with those of the isotropic refinement in table V, 3. The final values of the residuals for the observed reflections of $(NSF)_4$, $\alpha(NSOCl)_3$ and $(NSCl)_3$ are 5.6, 4.7 and 6.7 % respectively. Final coordinates are

given in table IV, 1, V, 1 and VI, 1 respectively. All computations were carried out on the digital computer ZEBRA. A survey of the programs used is given in appendix A.

The bond lengths and angles are given in table 1; only average values are listed for the crystallographically non-equivalent bond lengths, which agree within experimental error.

Table 1.
Bond lengths (Å) and valency angles.

	$(NSF)_4$		$\alpha(NSOCl)_3$		$(NSCl)_3$	
	value	e.s.d.	value	e.s.d.	value	e.s.d.
N-S	1.660, 1.540	0.015	1.569	0.005	1.605	0.004
S-Hal	1.602	0.009	2.003	0.003	2.150, 2.084	0.004
S-O			1.407	0.007		
N-S-N	111.7°	0.9°	113.0°	0.5°	113.4°	0.3°
S-N-S	123.9	0.9	122.0	0.5	123.9	0.3
N-S-O			111.9	0.4		
N-S-Hal	91.5, 106.2	0.6	106.3	0.3	113.7	0.3
O-S-Hal			107.0	0.4		

The $(NSF)_4$ molecule consists of a puckered ring with symmetry $\bar{4}$; the molecules are shown in fig. IV, and 5. The occurrence of unequal values of the bond angles N—S—F at a sulphur atom (91.5 and 106.2°) is sufficient to show that the two crystallographically independent S—N bonds in the molecule are different; in fact, the lengths of the S—N bonds alternate (1.540 and 1.660 Å). The fluorine atoms are located so as to give the most compact molecule.

The six-membered rings of $\alpha(NSOCl)_3$ and $(NSCl)_3$ have the chair form, the nitrogen atoms on the average being at a distance of 0.25 and 0.18 Å respectively from the plane through the sulphur atoms. All chlorine atoms are in axial positions (figure V, 4 and VI, 5). From the refinement in the centrosymmetric space groups, equal lengths for the S—N bonds in both molecules were found. Consideration of the valency angles showed that the possibility that equal values of the bonds would be simulated by an incorrect choice of the space groups is very improbable.

The difference in length between the two independent S—Cl bonds in $(NSCl)_3$ may be due to their different environments. One of the atoms of each bond has a strong interaction with atoms of neigh-

bouring molecules; some intermolecular distances are shorter than the sum of the van der Waals radii.

In chapter VII our results on (NS) ring systems are compared with the structures of the phosphonitrilic compounds. The length, 1.540 Å, of the shorter S—N bond in $(NSF)_4$ is approximately equal to the length predicted for a double bond from conventional radii, 1.56 Å (PAULING, 1960). The larger bond, 1.660 Å, is shorter than the „single" S—N bond, being 1.76 Å in sulfamic acid. From the bond lengths it follows that in $(NSF)_4$ delocalization of the π-electrons occurs to only a small extent. Since both the valency angles S—N—S and N—S—N are small in comparison with the corresponding angles P—N—P and N—P—N in the tetrameric phosphonitrilic molecules, the $(NS)_4$ ring in $(NSF)_4$ is more puckered than the $(NP)_4$ rings. The relatively small value of the angle S—N—S indicates that the nitrogen lone pair electrons do not contribute much to the π-bonding; delocalization of these electrons seems to be prevented by the lone pair electrons on the sulphur atoms. The relatively small value of the angle N—S—N may be due to the *p*-character of the sulphur hybrids used for the σ-bonds.

In $\alpha(NSOCl)_3$ and $(NSCl)_3$ the S—N bonds are appreciably shorter, 0.19 and 0.16 Å respectively, than the "single" S—N bond, which indicates double bond character involving d-orbitals of sulphur. Since the bond lengths in the bonds are equal, the extra bonds, presumably p_π-d_π bonds, must be completely delocalized. In both molecules the valency angles N—S—N are small in comparison with the angle N—P—N in $(NPCl_2)_3$. For $(NSCl)_3$ this will be due (as in $(NSF)_4$) to the *p*-character of the sulphur hybrids used for the σ-bonds and to the strong repulsion of the exocyclic lone pair. For $\alpha(NSOCl)_3$ it may be due to the strong repulsion of the double bonded oxygen atom.